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学位の種類	博　　士（理学）
学位記番号	富理工博甲第 92 号
学位授与年月日	平成 27 年 9 月 28 日
専　攻　名	地球生命環境科学専攻
学位授与の要件	富山大学学位規則第 3 条第 3 項該当
学位論文題目	Biogeochemical Study of Trace Elements in Surface Sediment from the Marginal Sea (East China Sea) to the Open-Ocean (Northwestern Pacific) （縁辺海（東シナ海）・外洋（北西太平洋）表層堆積物中の微量元素の生物地球化学的研究）
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Biogeochemical Study of Trace Elements in Surface Sediment from the Marginal Sea (East China Sea) to the Open-Ocean (Northwestern Pacific)

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Abstract

Surface sediment acts as the main repository and source of trace elements in the aquatic environment and plays an important role in the transport and storage. Understanding the source of trace elements and potential re-mineralization in the surface sediment can give us the integrated information of biogeochemical process compared with snapshot signal reflected by water column. The East China Sea (ECS), one of the largest marginal seas in the world, is an important terrestrial organic carbon sink with high productivity caused by large amounts of nutrients supplied from Changjiang River, coastal area of the Yellow Sea, and atmospheric input. Moreover, the outer shelf East China Sea (OSECS) is a bridge for water circulation and material transportation to other marginal sea (Yellow Sea and Japan Sea) and open ocean (Northwestern Pacific Ocean) through the Kuroshio Current (KC). Based on this information, three scientific questions were raised as follows 1) How the interaction of trace element with organic substances in the aquatic environment? 2) What is the source of trace elements in surface sediment in the OSECS and Northwestern Pacific Ocean (NwPO)? 3) How significant of potential re-mineralization of micronutrients in the surface sediment?

The surface sediment samples were carried out from the OSECS and NwPO in 2012 and 2013 by KT-12-25, KH-12-04, and KH-13-04 research cruises, respectively. A procedure proposed by the community Bureau of Reference (BCR) was used in this study to fractionate trace elements. It partitions, trace elements divided into four phases including carbonate, Fe/Mn oxides, organic matter and residual phase. Carbonate, oxide and organic matter are usually consider as indication of naturally marine biogenic, anthropogenic or authigenic source, while residual fraction represents the lithogenic source of trace elements. Trace elements concentration in each phases were measured by inductively coupled plasma-mass spectrometry (ICP-MS HP 4500, Agilent). Total organic carbon (TOC) and SiO_2 were observed by TOC analyzer (TOC-V_{CSH}, Shimadzu) and UV-Vis Spectrophotometer (UVmini-1240, Shimadzu), respectively.

In the freshwater and seawater, aquo complex ($Cd(H_2O)_6)^{2+}$) and chloro complex ($CdCl^+$ and $CdCl_2$) will be responsible for adsorption of Cd on organic substances. At 2 < pH <7, cadmium was in Cd(II) and ($Cd(H_2O)_6)^{+2}$ which was soluble in water, at 7< pH <10, part of the soluble Cd was precipitated as $Cd(OH)_2$, while at pH >10, all of the Cd were precipitated as $Cd(OH)_2$. In freshwater media, adsorption process through a single phase indicated that aquo and chloro complexes were simultaneously adsorbed on organic substances, while in seawater media occurs in 2 different phases indicated that aquo and chloro complexes individually adsorbed on organic substances.

Spatial distribution of trace elements, TOC, carbonate and SiO_2 showed that generally the southern area has higher concentration compared with middle and northern area of OSECS, likely biogenic source controls the distribution of trace elements. Based on the chemical fractionation, the trace elements in surface sediment of OSECS come from various sources including lithogenic, ocean biogenic and authigenic sources. The northern and the middle part, Pb, Mn, Zn and Cd were dominated by ocean biogenic (carbonate and organic phase) while Fe and Co were dominated by lithogenic (residual phase). The proportion of oxides fraction in the southern was bigger than the middle and the northern of OSECS indicated another geochemical processes influenced the fractionation compositions. Since this area was close with Okinawa where submarine volcanoes have been found, hydrothermal plume likely influenced trace elements composition. Potential re-mineralization of Fe, and Zn from surface sediment to the pore water or bottom water as micronutrient was bigger compare with atmospheric input in the southern of OSECS, implying that sediment may be an important micronutrient source to the northwestern Pacific Ocean through the Kuroshio Current. The mean concentration of the trace elements in surface sediment of the NwPO were in the following order: Fe > Mn > Zn > Pb > Co > Cd. Cadmium in all stations was dominated by carbonate phase, indicating biogenic and authigenic sources. Manganese and cobalt at the station close with the land were strongly influenced by lithogenic source, while at the open-ocean by authigenic source. Lead and zinc distributed in all phases indicated various sources like biogenic, authigenic and lithogenic source. Iron in all stations dominated in residual phase suggesting lithogenic source.

In the aquatic environment, aquo and chloro complexes will be responsible for adsorption of trace elements on organic substances. The adsorption processes of aquo and chloro complexes functioned simultaneously in freshwater and individually in seawater media. By using chemical fractionation, trace elements in surface sediment at the north and middle of OSECS are dominated by ocean biogenic and lithogenic, while southern area was largely influenced by hydrothermal plume source. Potential re-mineralization of Fe and Zn from surface sediment to the pore water or bottom water as micronutrient was higher than atmospheric input in the southern of OSECS, implying that surface sediment may be an important micronutrient source to the Japan Sea and the Northwestern Pacific Ocean.

[博士論文審査の結果の要旨]

当学位論文審査委員会は，審査論文「縁辺海（東シナ海）・外洋（北西太平洋）表層堆積物中の微量元素の生物地球化学的研究」（Biogeochemical Study of Trace Elements in Surface Sediment from the Marginal Sea (East China Sea) to the Open-Ocean (Northwestern Pacific)）を詳細に査読し，また平成27年8月12日の学位論文公聴会での精細な質疑応答において審査した。以下に審査および最終試験の結果を要約する。

海洋表層堆積物は海洋環境での微量元素の沈着と溶解を担い，海洋の物質循環系において重要な役割を果たしている。また，表層堆積物における微量元素（微量栄養塩）の分布状況は河川や大気などからの供給量と起源を記録し，底層海水への再生栄養塩の潜在的供給量推定が可能など，経時的に統合された生物地球化学的プロセスに関する情報を得ることができる。本研究は，世界最大の陸棚縁辺海で多量の CO_2 を吸収する東シナ海に着目し，陸源物質などの栄養塩が縁辺海へ供給される実態解明を目的としている。本研究では，①東シナ海の外部陸棚域，黒潮の中流から下流域，北西太平洋亜寒帯における表層堆積物中の微量元素の分布状況の把握，②各種微量元素の供給源同定と供給量試算，③堆積物中の潜在的再生栄養塩量の推定を行った。博士論文の構成は以下のとおりである。

第1章は，表層堆積物が海洋物質の循環系において重要な役割を果たし，東シナ海から西部北太平洋にかけて研究域とした本研究の目的と手法について概説した。第2章は，観測船を用いた試料の採取，BCR（Community Bureau of Reference）化学的分画法に関する微量元素などの分析・解析手法を記述した。第3章は，塩分の違いによる微量元素吸着性の変化を調べ，海水中ではアクア錯体とクロロ錯体はそれぞれ有機物に吸着することを記した。第4，5章は，東シナ海，北太平洋表層堆積物中の各種微量元素・全炭素・炭酸塩・Si などの空間分布とその要因・供給状況を調査・解析した。東シナ海において，微量元素が中部・北部と比べて南部陸棚域に高いことが分かった。これら微量元素分布の違いは砕屑物・海洋生物・海底熱水活動によるもので，中部・北部では，Pb・Mn・Zn・Cd は主に海洋生物生産(炭酸塩相および有機物相)を起源とするが，Fe・Co は主に岩石砕屑物（残留物相）に由来した。一方，南部では Fe・Mn 酸化物相の割合が大きく，海洋生物生産や岩石砕屑物以外に，近くの海底熱水活動の影響が示唆された。陸棚斜面に位置する観測域の底層水は黒潮中層水によって容易に有光層まで湧昇し，表層堆積物中の可溶性で熱水起源の Fe，Mn など微量栄養塩は，陸棚，また亜熱帯北太平洋，更に黒潮に沿って北西太平洋にも輸送される可能性を初めて示した。更に潜在的再生栄養塩として，表層堆積物中の Fe・Zn の間隙水や海底直上水への供給量を試算した結果，南部陸棚域においては，河川や大気による供給量よりも大きいことが分かった。

以上を総合的に判断した結果，本研究論文は，海洋地球化学・化学海洋学の研究分野において学術的に新しい知見を与えていることを認め，当審査委員会は博士の学位論文として十分な価値を有し，博士の学位を授与するに値すると判定した。